

**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants:	Ishiduka, et al.	Examiner:	Johnson, Connie P.
Application No.:	10/591,718	Group Art Unit:	1722
Confirmation No:	3280	Docket:	1608-7 PCT/US/RCE II
Filed:	September 5, 2006	Dated:	April 28, 2012
For:	POSITIVE-TYPE RESIST COMPOSITION FOR LIQUID IMMERSION LITHOGRAPHY AND METHOD FOR FORMING RESIST PATTERN		

Commissioner for Patents  
P.O. Box 1450  
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Dated: April 28, 2012

Signature: Marcy Mancuso /Marcy Mancuso/

**DECLARATION UNDER 37 C.F.R. § 1.132**

Sir:

Mr. Keita Ishiduka hereby declares and states as follows:

1. I am an inventor of the invention embodied in the above-identified patent application. This declaration is submitted in support of the patentability of the claimed invention.
2. I have been an employee of Tokyo Ohka Kogyo Co., Ltd., Japan, the assignee of the above-identified United States Patent Application and, since April 2002.

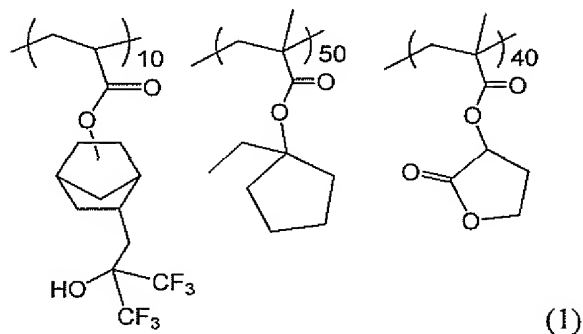
3. I have been engaged in research and development work relating to resist compositions and other related products of the company.
4. I have thoroughly read and understand the Office Action dated October 28, 2011 and the references cited therein. The invention as defined in the U.S. Patent Application Serial No. 10/591,718 has been rejected by the Examiner as being obvious over Japanese Publication 2003-040840 to Miyazawa et al. ("Miyazawa") in view of U.S. Patent No. 7,001,707 to Hatakeyama et al. ("Hatakeyama"), and U.S. Publication No. 2004/0259040 to Endo et al. ("Endo").
5. I submit data (Example 1) and Comparative Data (Comparative Examples 1-4) regarding the claimed resin composition.
6. The resin component included in the positive-type resist composition for liquid immersion lithography according to the present invention contains at least three types of constitutional units, i.e., a constitutional unit (a1), a constitutional unit (a2), and a constitutional unit (a4).
7. In this regard, the constitutional unit (a1) is induced from ester acrylate, and has a cyclic group to which a fluoro organic group is bound. Furthermore, the fluoro organic group has one unsubstituted alcoholic hydroxyl group. The constitutional unit (a2) is induced from a methacrylic ester having an acid dissociable, dissolution inhibiting group. The constitutional unit (a4) is induced from (meth)acrylic ester having a monocyclic or a polycyclic group containing lactone.
8. From the data presented below, it can be concluded that it would not be possible to arrive at a result of superior water repellency and patterning characteristics, and decreased influence of film loss until completing PEB from the disclosures of Miyazawa, Hatakeyama and Endo. The references Miyazawa, Hatakeyama and Endo, cited by the Examiner do not in any way disclose the constitutional unit (a4); therefore, a combination of at least three types of

constitutional units, the constitutional unit (a1), the constitutional unit (a2), and the constitutional unit (a4) is also not in any way disclosed.

9. Under my supervision and control, I have conducted tests on various samples, which showed that a resin (1) containing the three types of constitutional units described above was used exhibited superior water repellency and patterning characteristics, and decreased influence of film loss until completing PEB. On the other hand, Comparative Example 1 in which a resin (2) not containing the constitutional unit (a1) was used exhibited inferior water repellency, and thus is not suited for liquid immersion lithography process due to failure in slippage of water droplets. In addition, increased influence of film loss until completing PEB was exhibited. Similarly, Comparative Example 2 in which a resin (3) that is similar to the resin (1) but has two unsubstituted alcoholic hydroxyl groups was used exhibited inferior water repellency, and thus is not suited for liquid immersion lithography process due to failure in slippage of water droplets. Additionally, Comparative Example 3 in which a resin (4) not containing the constitutional unit (a4) was used failed to form a 100  $\mu\text{m}$  line pattern due to inferior patterning characteristics. Moreover, Comparative Example 4 in which a resin (5) that is similar to the resin (1) but does not have a cyclic group was used exhibited increased influence of film loss until completing PEB.

#### Example 1

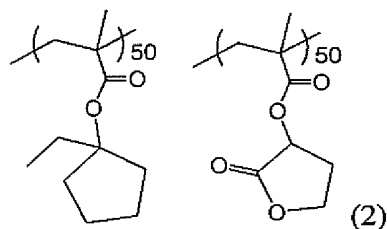
A resin, the alkali-solubility of which increases by action of an acid, an acid generator, and a nitrogen-containing organic compound were uniformly dissolved in an organic solvent to prepare a resist composition. As the resin, 100 parts by mass of a resin (1) represented by the following formula were used. The number added to the side of each constitutional unit represents proportion (mol%) of each constitutional unit.



As the acid generator, 5 parts by mass of triphenylsulfonium nonafluorobutanesulfonate were used. As the nitrogen-containing organic compound, 0.45 parts by mass of triethanolamine were used. As the organic solvent, 1600 parts by mass of a mixed solvent of propylene glycol monomethyl ether acetate and ethyl lactate (mass ratio: 6:4) were used.

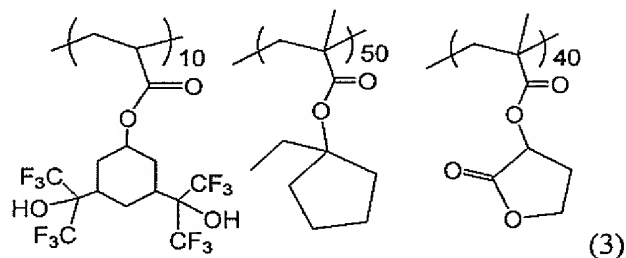
#### Comparative Example 1

A resist composition was prepared in a similar manner to Example 1 except that a resin (2) represented by the following formula was used in place of the resin (1).



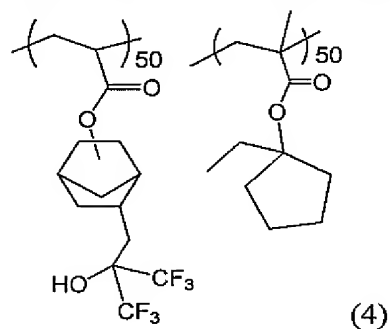
#### Comparative Example 2

A resist composition was prepared in a similar manner to Example 1 except that a resin (3) represented by the following formula was used in place of the resin (1).



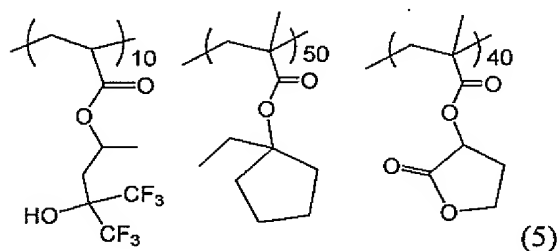
### Comparative Example 3

A resist composition was prepared in a similar manner to Example 1 except that a resin (4) represented by the following formula was used in place of the resin (1).



### Comparative Example 4

A resist composition was prepared in a similar manner to Example 1 except that a resin (5) represented by the following formula was used in place of the resin (1).



## **2. Evaluation**

### **Water Repellency**

On a silicon wafer which had been subjected to a HMDS treatment was applied each of the resist compositions of Example 1, and Comparative Examples 1 to 4, and baked on a hot plate at 90°C for 60 sec to form a resist film having a film thickness of 80 nm. Then, 50  $\mu$ L of water was dropped on the surface of the resist film, and a contact angle of the droplet was determined using “DROP MASTER-700” (product name, manufactured by Kyowa Interface Science Co., LTD.).

### **Results**

When the resist compositions of Example 1, and Comparative Examples 3 and 4 were used, sufficiently high water repellency of the surface of the resist film was shown. Whereas, when the resist compositions of Comparative Examples 1 and 2 were used, low water repellency of the surface of the resist film was shown, indicating that the droplet failed to slip.

### **Patterning Characteristics**

An organic anti-reflection coating composition “ARC29” (trade name, manufactured by Brewer Science) was applied on a silicon wafer, and an organic anti-reflection coating film having a film thickness of 82 nm was formed by baking on a hot plate at 205°C for 60 sec. Subsequently, each of the resist compositions of Example 1, and Comparative Examples 1, 3 and 4 was applied on the anti-reflection coating film, and a resist film having a film thickness of 80 nm was formed by baking on a hot plate at 90°C for 60 sec. Next, the resist film was selectively irradiated through a mask with an ArF excimer laser (193 nm) by means of an ArF exposure system “NSR-S302A” (product name, manufactured by Nikon Corporation; NA (numerical aperture) = 0.60, 2/3 annular illumination). The mask employed corresponded to a resist pattern (line-and-space pattern) with a line width of 150 nm or 100 nm, and a pitch of 300 nm. Then, a process of post-exposure baking (PEB) at 80°C was carried out for 60 sec, followed by an alkali development treatment with a 2.38% by mass aqueous tetramethylammonium hydroxide (TMAH) solution “NMD-3” (trade name, manufactured by Tokyo Ohka Kogyo Co., Ltd.) at 23°C for 30 sec.

Thereafter, the resist film was rinsed with pure water for 30 sec, and a process of post baking was carried out at 100°C for 60 sec.

### **Results**

When the resist compositions of Example 1, and Comparative Examples 1 and 4 were used, formation of both the resist pattern with a line width of 150 nm and the resist pattern with a line width of 100 nm was enabled. On the other hand, when the resist composition of Comparative Example 3 was used, formation of the resist pattern with a line width of 150 nm was enabled, whereas formation of the resist pattern with a line width of 100 nm failed since the resist pattern peeled off from the wafer.

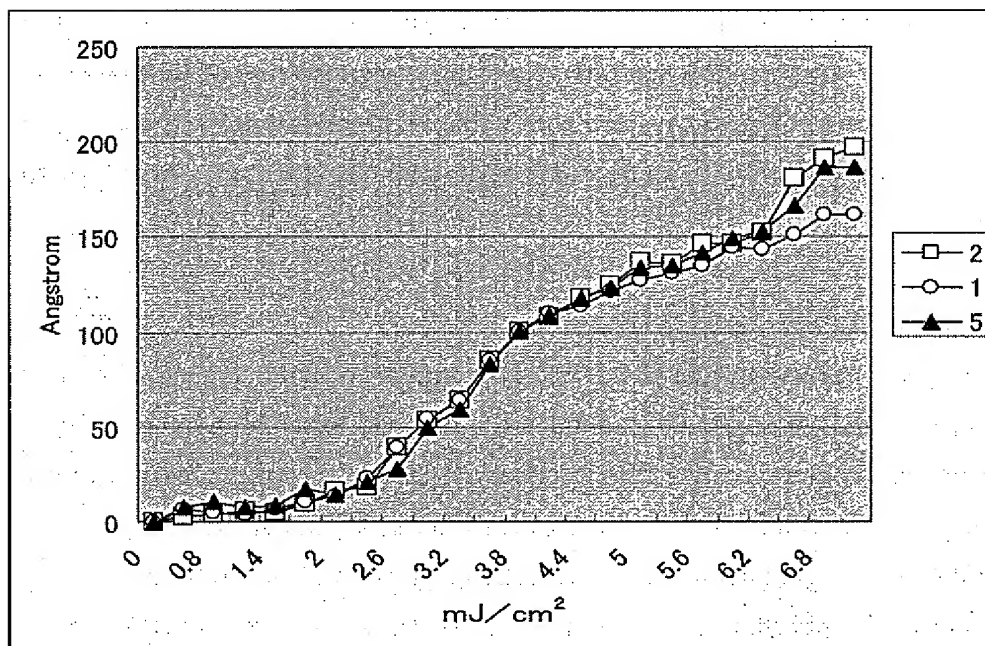
### **Influences of Film Loss Until Completing PEB**

On a silicon wafer which had been subjected to a HMDS treatment was applied each of the resist compositions of Example 1, and Comparative Examples 1 and 4, and baked on a hot plate at 90°C for 60 sec to form a resist film having a film thickness of 80 nm. Next, the resist film was irradiated without using a mask with an ArF excimer laser (193 nm) by means of an ArF exposure system “NSR-S302A” (product name, manufactured by Nikon Corporation; NA (numerical aperture) = 0.60, 2/3 annular illumination). In this process, the exposure dose was changed from 0.5 mJ/cm<sup>2</sup>, with 0.3 mJ/cm<sup>2</sup> increment. Subsequently, a process of post-exposure baking (PEB) at 80°C was carried out for 60 sec.

Thereafter, the film thickness when PEB was completed was measured using “Nanospec 6100A” (product name, manufactured by Nanometrics Incorporated), and the difference from the film thickness when applied was determined as “film loss quantity”. The results are shown in the graph below. In this graph, the ordinate represents the film loss quantity (Å), and the abscissa represents the exposure dose (mJ/cm<sup>2</sup>).

### Results

As can be seen from the graph, it was ascertained that when the resist compositions of Comparative Examples 1 and 4 were used, greater film loss quantities were observed in the range of the exposure dose beyond about  $6.2 \text{ mJ/cm}^2$ , as compared with the case in which the resist composition of Example 1 was used.



### Conclusion:

From the foregoing results, it is confirmed that the resist composition of Example 1 containing the resin (1) was superior in water repellency and patterning characteristics, indicating less influence of the film loss until completing PEB.

Based upon my understandings of the teachings of the cited references, and my knowledge of known scientific principles in the field, there is no prior art disclosure which, at the time of our invention, would have suggested the use of constitutional unit (a4); therefore, a combination of at least three types of constitutional units, the constitutional unit (a1), the constitutional unit (a2),



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and the constitutional unit (a4) is also not in any way disclosed. Thus, I believe that the effects as described above achievable by using the three types of constitutional units in combination could not have been conceived in view of Miyazawa, Hatakeyama, or Endo.

I declare the foregoing to be true and accurate to the best of my knowledge under penalty of law.

Dated: 2012. 4. 24

Signed: Keita Ishiduka.  
Mr. Keita Ishiduka.

Application No. 10/591,718  
Applicants: Ishiduka et al.  
Dated: DRAFT  
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